

TODD ET AL.

Group Art Unit: 1712

Examiner: **ZIMMER, MARC S.**

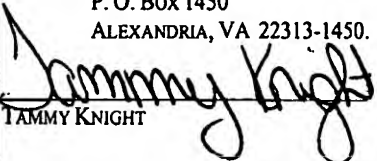
**Atty. Docket No: 2001-IP-005443U2**


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EXAMINER: ZIMMER, MARC S.

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**DECLARATION PURSUANT TO 37 C.F.R. § 1.131**

2. We are the inventors of the subject matter of the above-referenced application, entitled, "Compositions and Methods for Reducing the Viscosity of a Fluid" (the "Patent Application").

3. The Examiner rejected claims 1, 2, 7-9, 14-16, 21, 22, 27, and 30 (the "Claims") of the Patent Application in an Office Action mailed March 6, 2006, based, in whole or in part, on U.S. Patent Application Publication No. 2005/0028976 by Philip D. Nguyen ("the Nguyen Application") that was filed on August 5, 2003.

4. Sometime prior to August 5, 2003, we, the undersigned, developed an understanding and appreciation of the subject matter as described in the Patent Application and Claims, as evidenced by an invention disclosure form attached as Exhibit A, which is described below.

5. As an example, we, the undersigned, reduced to practice the subject matter of the Patent Application and Claims as evidenced by attached Exhibit A. The methods shown in Exhibit A include at least a method of reducing the pH of a servicing fluid comprising the steps of: providing a crosslinked, viscous servicing fluid comprising an acid-releasing degradable material; allowing the acid-releasing degradable material to produce an acid; and allowing a pH of the servicing fluid to be reduced. Exhibit A includes experimental results, which with the accompanying textual description, show a reduction to practice of this subject matter.

6. The acts referred to in paragraphs 4 and 5 were carried out in the United States prior to August 5, 2003.

7. We hereby declare that all statements made herein and of our knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Bradley L. Todd  
Bradley L. Todd

7-18-2006  
Date

Billy F. Slabaugh  
Billy F. Slabaugh

7-6-2006  
Date

Trinidad Munoz, Jr.  
Trinidad Munoz, Jr.

7-24-2006  
Date

# **EXHIBIT A**

2001-IP-005443

TITLE: Lactides for use as Delayed pH Reduction

## FULL NAME OF FIRST JOINT INVENTOR

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Address: Street City State Zip

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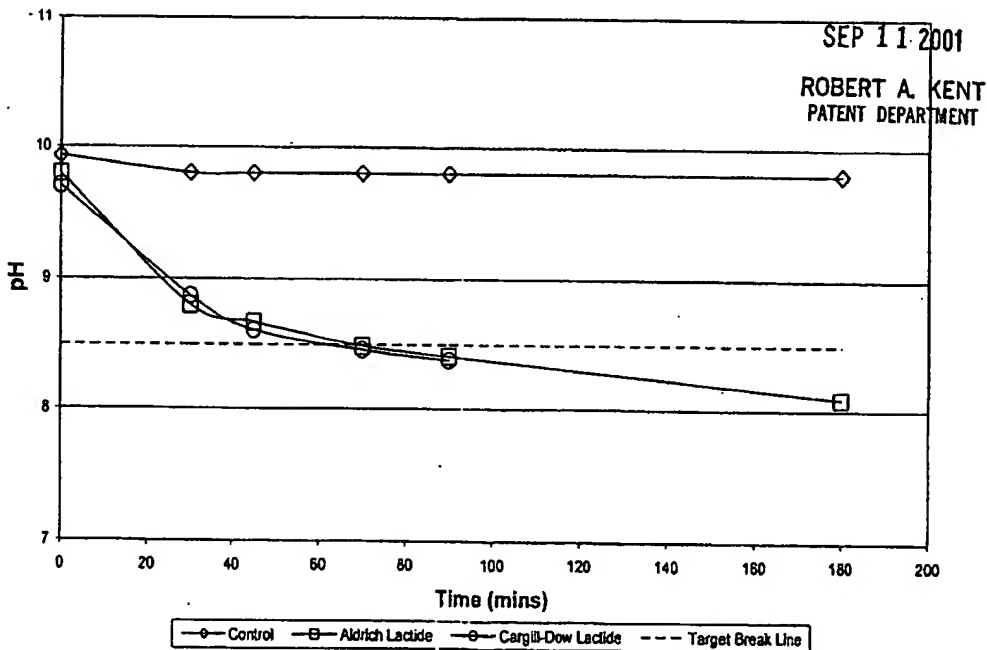
Description of Invention: Give brief description of invention, and where possible a sketch. Do not write on back of this sheet. If additional space is necessary, use additional disclosure sheets (R&S 2311) and number consecutively. Sign and date each sheet and have each witnessed. Witnesses must be persons capable of understanding invention. If invented prior to date on this sheet, give full details - date, to whom disclosed, identify drawings, if any, etc. If used in the field, specify for what company and designate well and date.

Lactides are cyclic, intermolecular double esters formed from  $\alpha$ -hydroxy acids. The term can also be used for the particular double ester of lactic acid. Likewise, glycolide is a term used for the cyclic double ester of glycolic acid. When these materials are placed in an aqueous media, they will eventually hydrolyze to the parent  $\alpha$ -hydroxy acid. The rate at which they hydrolyze produces a controlled delayed reduction in pH useful as a breaker in fracturing fluids.

The rate of pH reduction was tested with both reagent grade (Aldrich) and agricultural grade (Cargill-Dow) at 130 degrees F on a HPF fluid. See figure below for pH reduction. For this fluid, a pH of about 8.5 causes the fluid to break. The figure on the next page shows the Model 50 break of an HPF fluid at 150F with 30 #/M lactide.

## Lactide Break of HPF Fluid

RECEIVED

Signed at Duncan OK this 10 day of Sept, 2001Signature of Inventor  
Brad ToddSigned at Duncan OK this 10 day of September, 2001Signature of Inventor  
Billy Slabaugh

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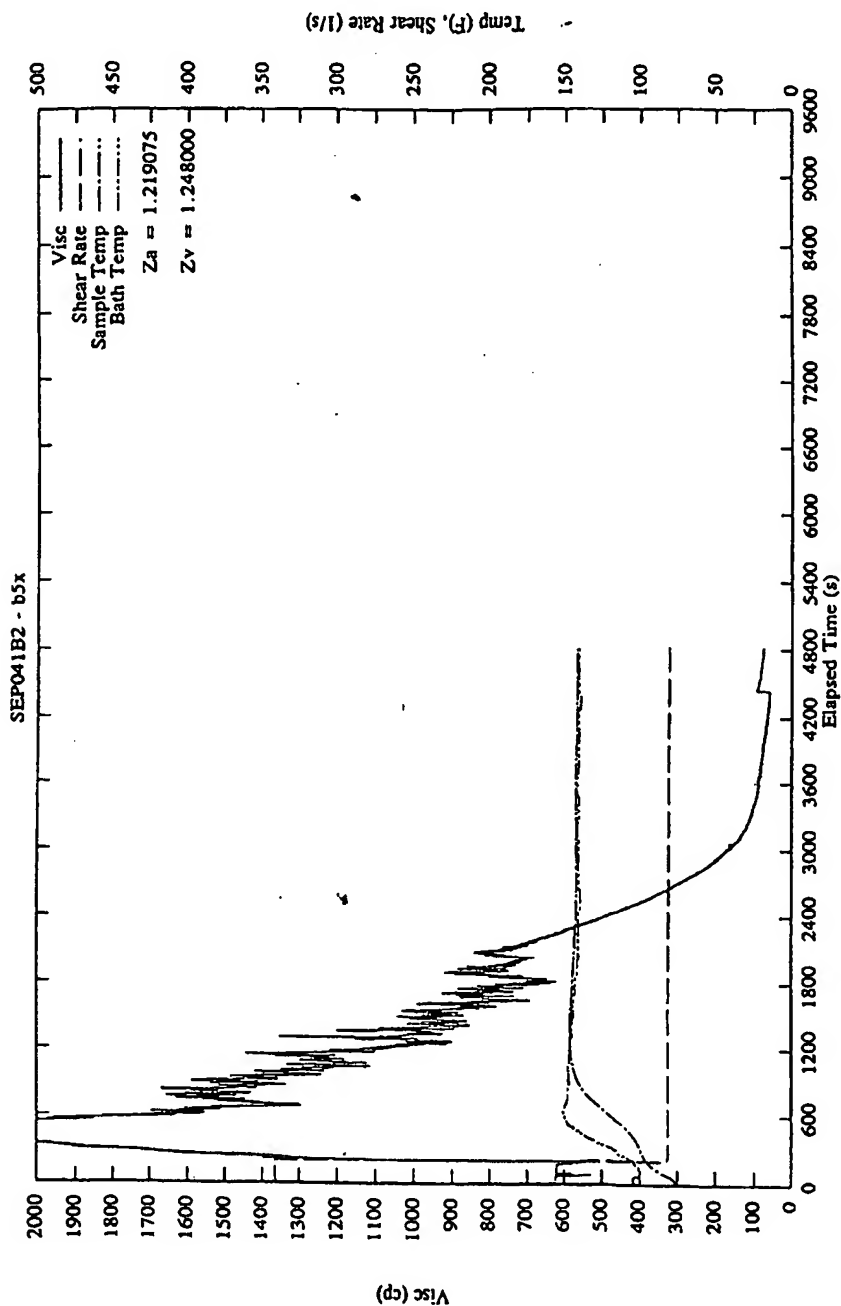
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[Signature]

9-11-01

Please forward immediately to: Halliburton Services, Patent/Legal, Duncan, OK 73536-0102

Date

TITLE: Lactides for use as Delayed pH Reduction



Signed at Duncan, OK this 10 day of Sept, 2001

Head Jodel  
Signature of Inventor

Signed at Duncan, OK this 10 day of September, 2001

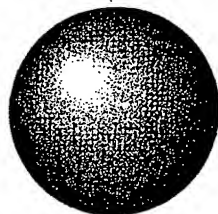
Bill Dyer  
Signature of Inventor

Explained to and Understood by Me:

Daniel Allen  
Signature of Witness

9-11-01

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THIRD EDITION

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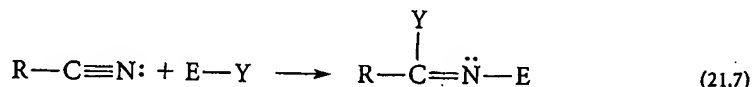


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of an acid chloride, the  $\text{—OR}$  of an ester, and so on; this group is substituted by another group  $\text{—Y}$ . This is precisely the same type of reaction as esterification of carboxylic acids ( $\text{—X} = \text{—OH}$ ,  $\text{E—Y} = \text{H—OCH}_3$ ; Sec. 20.8A). Acyl substitution reactions of carboxylic acid derivatives are the major focus of this chapter.

Although nitriles are not carbonyl compounds, the  $\text{C}\equiv\text{N}$  bond behaves chemically much like a carbonyl group. For example, a typical reaction of nitriles is *addition*.



(Compare this reaction with addition to the carbonyl group of an aldehyde or ketone.) Although the resulting addition products are stable in some cases, in most situations they react further.

Like aldehydes and ketones, carboxylic acid derivatives undergo certain reactions involving the  $\alpha$ -carbon. The  $\alpha$ -carbon reactions of all carbonyl compounds are grouped together in Chapter 22. The reactivity of amides at nitrogen is discussed in Sec. 23.11C.

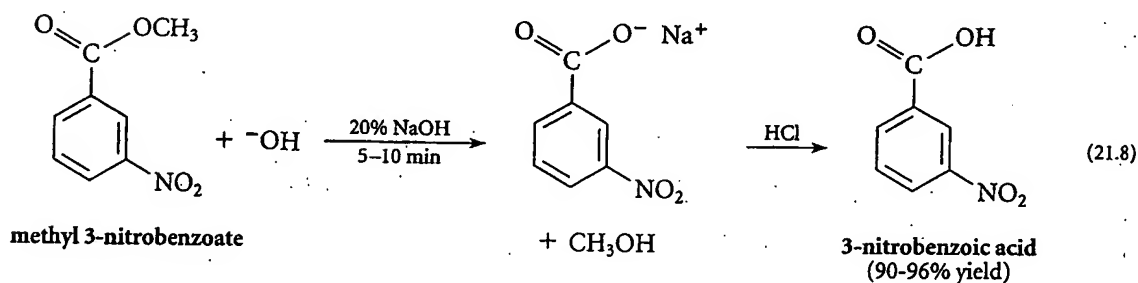


## Hydrolysis of Carboxylic Acid Derivatives

All carboxylic acid derivatives have in common the fact that they undergo *hydrolysis* (a cleavage reaction with water) to yield carboxylic acids.

### A. Hydrolysis of Esters

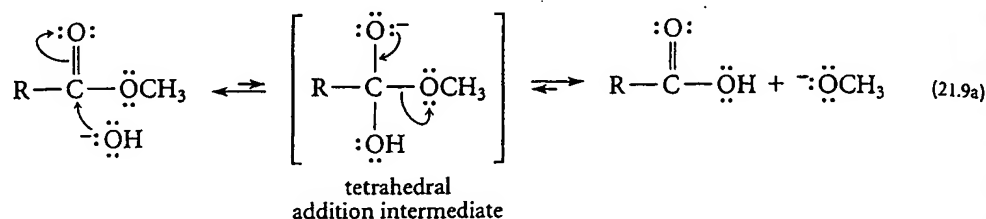
**Saponification of Esters** One of the most important reactions of esters is the cleavage reaction with hydroxide ion to yield a carboxylate salt and an alcohol. The carboxylic acid itself is formed when a strong acid is subsequently added to the reaction mixture.



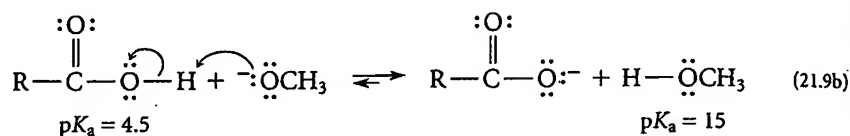
Ester hydrolysis in aqueous hydroxide is called *saponification* because it is used in the production of soaps from fats (Sec. 21.12B). Despite its association with fatty-acid esters, the term *saponification* is sometimes used to refer to hydrolysis in base of any acid derivative.

The mechanism of ester saponification involves attack by the nucleophilic hydroxide anion to give a tetrahedral addition intermediate from which an alkoxide ion is expelled.





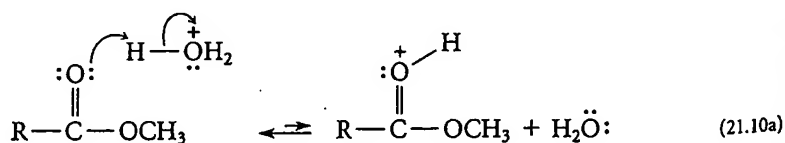
The alkoxide ion thus formed (methoxide in the above example) reacts with the acid to give the carboxylate salt and the alcohol.



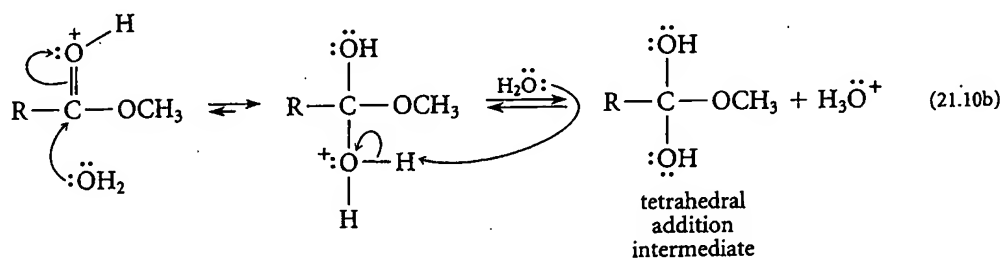
The equilibrium in this reaction lies far to the right because the carboxylic acid is a much stronger acid than methanol. LeChatelier's principle operates: the reaction in Eq. 21.9b removes the carboxylic acid from the equilibrium in Eq. 21.9a as its salt and thus drives the hydrolysis to completion. Hence, *saponification is effectively irreversible*. Although an excess of hydroxide ion is often used as a matter of convenience, many esters can be saponified with just one equivalent of  $\text{OH}^-$ . Saponification can also be carried out in an alcohol solvent, even though an alcohol is one of the products of the reaction. If saponification were reversible, an alcohol could not be used as the solvent, because the equilibrium would be driven towards starting materials.

**Acid-Catalyzed Ester Hydrolysis** Because esterification of an acid with an alcohol is a reversible reaction (Sec. 20.8A), esters can be hydrolyzed to carboxylic acids in aqueous solutions of strong acids. In most cases this reaction is slow and must be carried out with an excess of water, in which most esters are insoluble. Saponification, followed by acidification, is a much more convenient method for hydrolysis of most esters because it is faster, it is irreversible, and it can be carried out not only in water, but also in a variety of solvents—even alcohols.

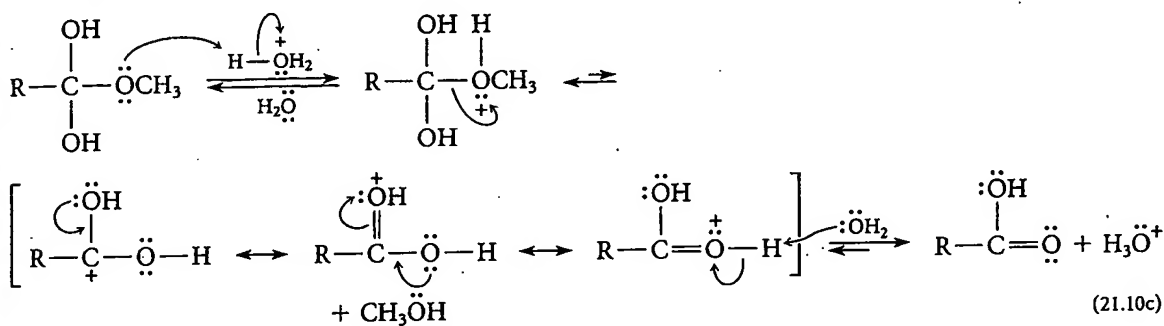
As expected from the principle of microscopic reversibility (Sec. 10.1), the mechanism of acid-catalyzed hydrolysis is the exact reverse of the mechanism of acid-catalyzed esterification (Sec. 20.8A). The ester is first protonated by the acid catalyst:



As in other acid-catalyzed reactions at the carbonyl group, protonation makes the carbonyl carbon more electrophilic by making the carbonyl oxygen a better acceptor of electrons. Water, acting as a nucleophile, attacks the carbonyl carbon and then loses a proton to give the tetrahedral addition intermediate:



Protonation of the leaving oxygen converts it into a better leaving group. Loss of this group gives a protonated carboxylic acid, from which a proton is removed to give the carboxylic acid itself.



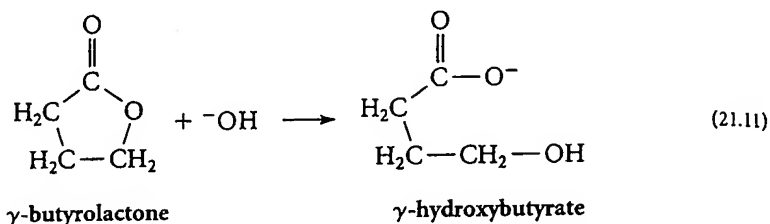
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Mechanism of Ester  
Hydrolysis

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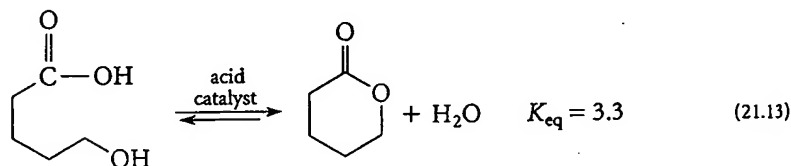
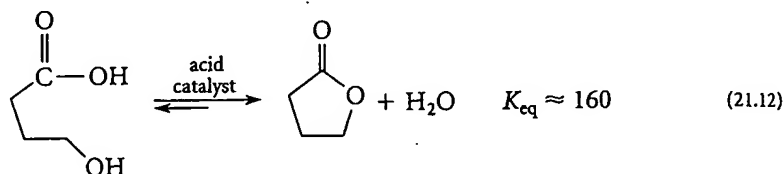
Let's summarize the important differences between acid-catalyzed ester hydrolysis and ester saponification. First, in acid-catalyzed hydrolysis, the carbonyl carbon can be attacked by the relatively weak nucleophile water because the carbonyl oxygen is protonated. In base, the carbonyl oxygen is not protonated; hence, a much stronger base than water, namely, hydroxide ion, is required to attack the carbonyl carbon. Second, acid catalyzes ester hydrolysis, but base is *not* a catalyst because it is consumed by the reaction in Eq. 21.9b. Finally, acid-catalyzed ester hydrolysis is reversible, but saponification is irreversible, again because of the ionization in Eq. 21.9b.

Ester hydrolysis and saponification are both examples of *acyl substitution* (Sec. 21.6). Specifically, the mechanisms of these reactions are classified as **nucleophilic acyl substitution** mechanisms. In a nucleophilic acyl substitution reaction, the substituting group attacks the carbonyl carbon as a nucleophile. This nucleophile is  $\text{OH}^-$  in saponification, and  $\text{H}_2\text{O}$  in acid-catalyzed hydrolysis; each group displaces, or substitutes for, the  $\text{OR}$  group of the ester. With the exception of the reactions of nitriles, most of the reactions in the remainder of this chapter are nucleophilic acyl substitution reactions.

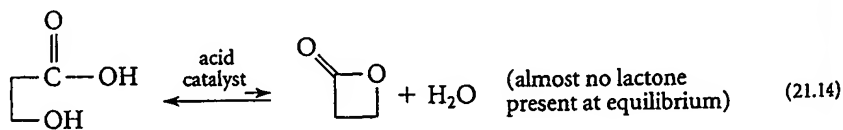
**Hydrolysis and Formation of Lactones** Because lactones are cyclic esters, they undergo many of the reactions of esters, including saponification. Saponification converts a lactone completely into the salt of the corresponding hydroxy acid.



Upon acidification, the hydroxy acid forms. However, if a hydroxy acid is allowed to stand in acidic solution, it comes to equilibrium with the corresponding lactone. The formation of a lactone from a hydroxy acid is nothing more than an intramolecular esterification (an esterification within the same molecule) and, like esterification, the lactonization equilibrium is acid-catalyzed.

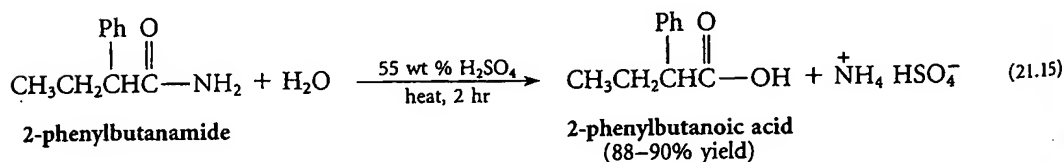


As the examples in Eqs. 21.12 and 21.13 illustrate, lactones containing five- and six-membered rings are favored at equilibrium over their corresponding hydroxy acids. Although lactones with ring sizes smaller than five or larger than six are well known, they are less stable than their corresponding hydroxy acids. Consequently, the lactonization equilibria for these compounds favor instead the hydroxy acids.

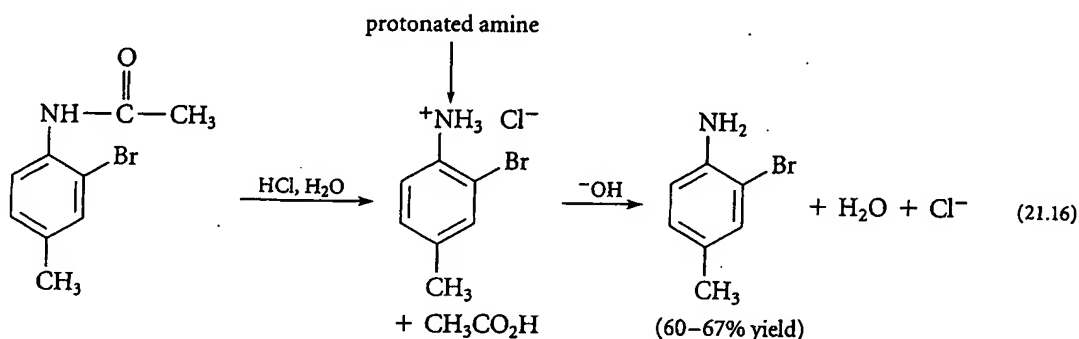


## B. Hydrolysis of Amides

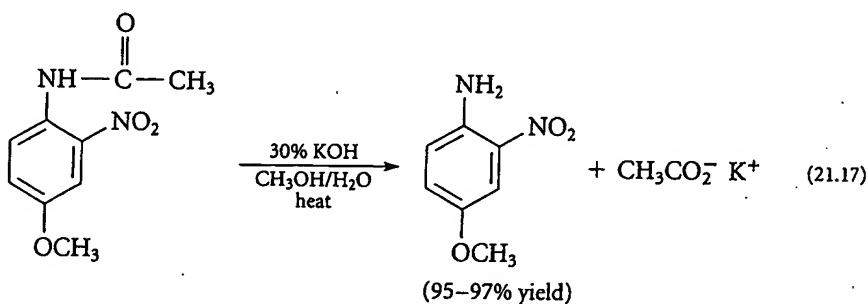
Amides can be hydrolyzed to carboxylic acids and ammonia or amines by heating them in acidic or basic solution.



In acid, protonation of the ammonia or amine by-product drives the hydrolysis equilibrium to completion. The amine can be isolated, if desired, by addition of base to the reaction mixture following hydrolysis, as in the following example.



Hydrolysis of amides in base is analogous to saponification of esters. In base, the reaction is driven to completion by formation of the carboxylic acid salt.



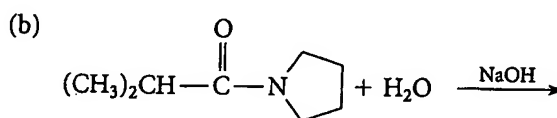
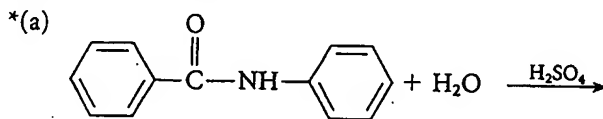
The conditions for both acid- and base-promoted amide hydrolysis are considerably more severe than the corresponding reactions of esters. That is, amides are considerably *less reactive* than esters. The relative reactivities of carboxylic acid derivatives are discussed in Sec. 21.7E.

The mechanisms of amide hydrolysis are typical nucleophilic acyl substitution mechanisms; you are asked to explore this point in Problem 21.10.

PROBLEM

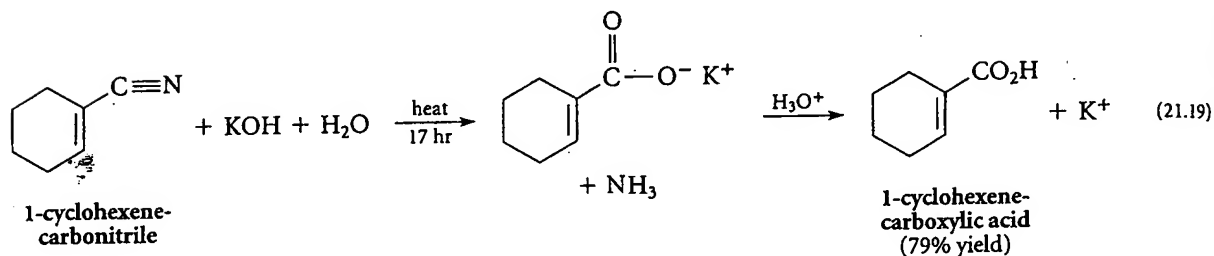
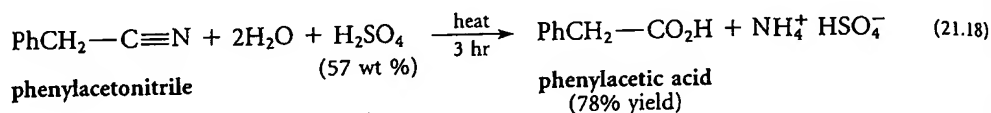
21.10 Show in detail the hydrolysis mechanism of *N*-methylbenzamide \*(a) in acidic solution; (b) in aqueous NaOH. Assume that each mechanism involves a tetrahedral addition intermediate.

21.11 Give the structures of the hydrolysis products that result from each of the following reactions.



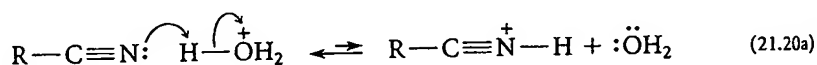
### C. Hydrolysis of Nitriles

Nitriles are hydrolyzed to carboxylic acids and ammonia by heating them in acidic or basic solution.

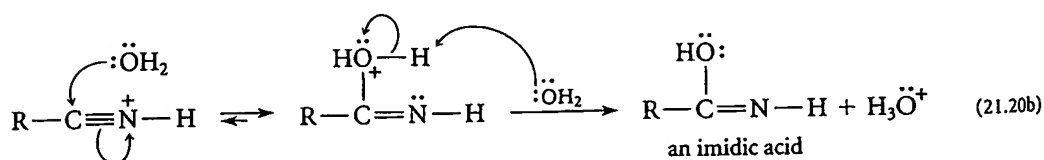


Nitriles hydrolyze more slowly than esters and amides. Consequently, the conditions required for the hydrolysis of nitriles are correspondingly more severe.

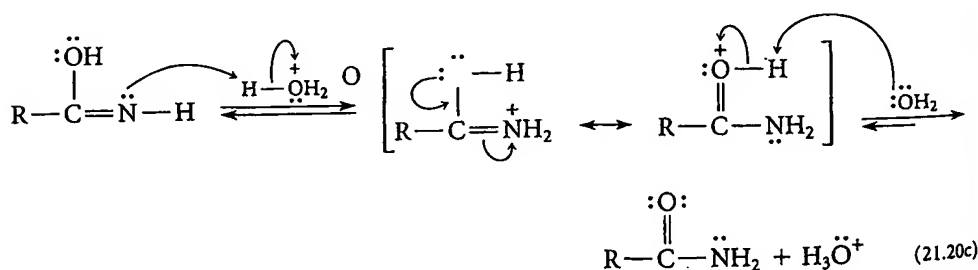
The mechanism of nitrile hydrolysis in acidic solution involves, first, protonation of the nitrogen (Sec. 21.5):



This protonation makes the nitrile carbon much more electrophilic, just as protonation of a carbonyl oxygen makes a carbonyl carbon more electrophilic. Attack of the nucleophile water on the nitrile carbon and loss of a proton gives an intermediate called an *imidic acid*.



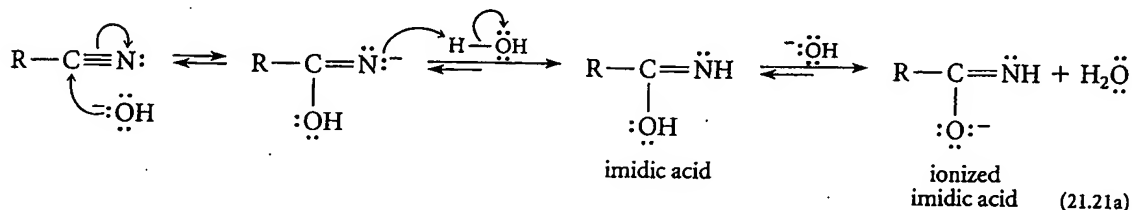
The imidic acid is unstable and is converted under the reaction conditions into an amide:



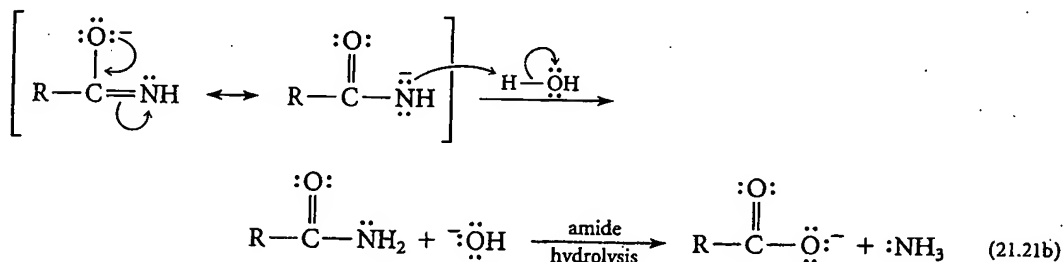
Because amide hydrolysis is faster than nitrile hydrolysis, the amide formed in Eq. 21.20c does not survive under the vigorous conditions of nitrile hydrolysis, and is hydrolyzed to a carboxylic acid and ammonium ion, as discussed in Sec. 21.7B. Thus, the ultimate product of nitrile hydrolysis in acid is a carboxylic acid.

Notice that nitriles behave mechanistically much like carbonyl compounds. Compare, for example, the mechanism of acid-promoted nitrile hydrolysis in Eqs. 21.20a and b with that for the acid-catalyzed hydration of an aldehyde or ketone (Sec. 19.7A). In both mechanisms, an electronegative atom is protonated (nitrogen of the  $C\equiv N$  bond, or oxygen of the  $C=O$  bond), and water attacks the carbon of the resulting cation.

The parallel between nitrile and carbonyl chemistry is further illustrated by the hydrolysis of nitriles in base. The nitrile group, like a carbonyl group, is attacked by basic nucleophiles and, as a result, the electronegative nitrogen assumes a negative charge. Proton transfer gives an imidic acid (which, like a carboxylic acid, ionizes in base).

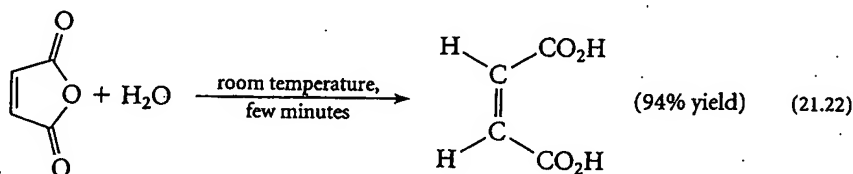


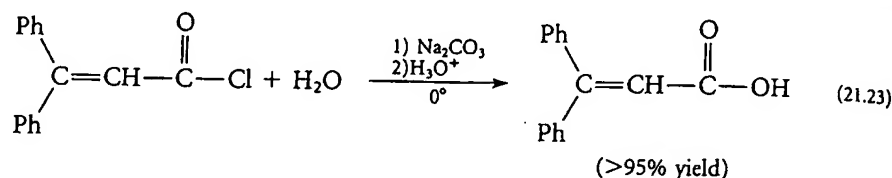
As in acid-promoted hydrolysis, the imidic acid reacts further to give the corresponding amide, which, in turn, hydrolyzes under the reaction conditions to the carboxylate salt of the corresponding carboxylic acid (Sec. 21.7B).



## D. Hydrolysis of Acid Chlorides and Anhydrides

Acid chlorides and anhydrides react *rapidly* with water, even in the absence of acid or base catalysts.



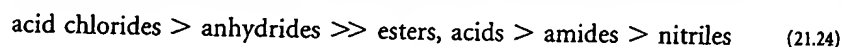


However, the hydrolysis reactions of acid chlorides and anhydrides are almost never used for the preparation of carboxylic acids, because these derivatives are themselves usually prepared from acids (Sec. 20.9). Rather, these reactions serve as reminders that if samples of acid chlorides and anhydrides are allowed to come into contact with moisture they will rapidly become contaminated with the corresponding carboxylic acids.

### E. Mechanisms and Reactivity in Nucleophilic Acyl Substitution Reactions

As you've seen, all carboxylic acid derivatives can be hydrolyzed to carboxylic acids; however, the *conditions* under which the different derivatives are hydrolyzed differ considerably. Hydrolysis reactions of amides and nitriles require heat as well as acid or base; hydrolysis reactions of esters require acid or base, but require heating only briefly, if at all; and hydrolysis reactions of acid chlorides and anhydrides occur rapidly at room temperature even in the absence of acid and base. These trends in reactivity, which are observed not only in hydrolysis, but in *all* nucleophilic acyl substitution reactions, can be summarized as follows:

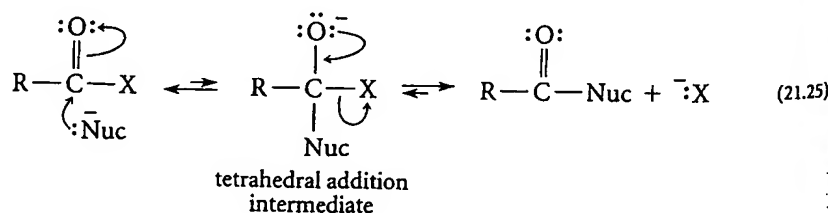
*Reactivities of carboxylic acid derivatives in nucleophilic acyl substitution reactions:*



(The reactions of nitriles are additions, not substitutions, but are included for comparison.)

The practical significance of this reactivity order is that selective reactions are possible. In other words, an ester can be hydrolyzed under conditions that will leave an amide in the same molecule unaffected; likewise, nucleophilic substitution reactions on an acid chloride can be carried out under conditions that will leave an ester group unaffected.

Understanding the trends in relative reactivity requires, first, an understanding of the mechanisms by which nucleophilic acyl substitution reactions take place. (The reactivity of nitriles is considered later.) For the sake of simplicity, imagine a reaction of a nucleophile,  $\text{:Nuc}^-$ , with a carboxylic acid derivative containing a leaving group X under neutral or basic conditions. The substitution reaction involves formation of a tetrahedral addition intermediate.



Which step is rate-limiting depends on the carbonyl compound and the nucleophile.